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PATENT SPECIFICATION

674,137

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COMPLETE SPECIFICATION.

Improvements relating to Ethyl Silicate and to its Use in the Production of Refractory Materials.

We, MONSANTO CHEMICALS LIMITED a, British Company, of 8, Waterloo Place, London, S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement :—

This invention relates to an ethyl silicate of a special composition particularly suitable for use in the production of refractory materials, especially in precision casting, and to the use of this ethyl silicate for the purpose.

Refractory materials of good quality can be obtained using ethyl silicate as a binding agent by mixing aqueous or more usually aqueous alcoholic ethyl silicate (to which a hydrolysing agent for the ethyl silicate has been added) with a refractory substance such as calcined fireclay to form a slurry or mix, shaping this to the desired form, a brick or mould for instance, allowing the ethyl silicate to gel and thus harden the shaped article, and firing the product at a high temperature at which the gel is converted to silica. This appears to cement the particles of the refractory substance together to form a firm product. Attention is drawn to Specifications Nos. 575,734, 604,698, 621,737 and 639,802.

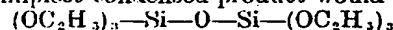
The technique is of particular value in the "lost wax" process of precision casting. In this process a wax replica is made of the casting required and this is embedded in a slurry or mix of a refractory substance and the ethyl silicate, which is allowed to set round the wax by gelling of the ethyl silicate. The mass is then fired to melt the wax and leave a refractory mould in which molten metal can be poured. It is not altogether necessary to use wax, and other substances,

such as fusible plastics, are also suitable : in referring to the "lost wax" process in this Specification the use of these other substances is included also. An illustration of the technique is given in Specification No. 660,604, and reference is also made to Dunlop's article in the Foundry Trade Journal, 75, (1945), 107.

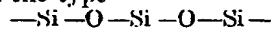
Although in this connection ethyl silicate is referred to without qualification, there are in fact a number of different chemical forms in which the ethyl silicate can be used. Ethyl silicate is normally prepared by the action of silicon tetrachloride on ethyl alcohol, and the chemical constitution of the product depends on such factors as the amount of water present when this reaction takes place. Thus if absolute alcohol is employed and the conditions are anhydrous the product will be ethyl orthosilicate of the formula



whereas if a quantity of water is present condensed products are formed, possibly owing to partial hydrolysis of the orthosilicate which may first be formed. Thus the simplest condensed product would be



and many other condensed forms containing systems of the type



are possible. If alcohol containing say 5% of water by weight is used, a mixture of ethyl silicates is formed varying from the orthosilicate to more complex condensates, each of course containing a higher proportion of silicon than the orthosilicate itself.

It has now been found that improved results are obtained in preparing the refractory materials if there is used an ethyl silicate having such a composition that on distilling at atmospheric pressure 8—16%

of it by volume distills up to 180° C. and 30—55% of it above 180° C., when the distillation is carried out without any substantial reflux and is continued to the point where the residue is a glue-like mass which on further heating merely breaks down to give lower boiling products. This point can readily be seen in practice by a drop in the temperature of the distilling vapours on account of these lower boiling degradation products. The fraction distilling up to 180° C. appears to be mainly ethyl orthosilicate, which boils at about 164° C., and the second fraction appears to be mainly the condensed products containing two and three silicon atoms respectively.

It is necessary for the distillation to be carried out without any substantial reflux for the reason that otherwise the composition of the ethyl silicate is liable to change during the distillation to an extent which interferes with the test. A suitable apparatus to ensure that there is no substantial reflux is that described in Standard D 86—46 of the American Society for Testing Materials in connection with the distillation of petroleum products.

By using an ethyl silicate of this particular composition in the production of the refractory materials two notable results are obtained. The gelling time of the slurry or mix containing the ethyl silicate is reasonably short, perhaps less than two and a half hours, and also a good strength is obtained in the formed refractory material ready for firing. The precise time of gelation will of course depend on the conditions, and whether for instance the hydrolysing agent used is an acid such as hydrochloric acid (see Cogan and Setterstrom, Ind. Eng. Chem., 39, (1947), 1364) or one of the organic bases described in Specifications Nos. 575,752 and 612,622, but it is very desirable for this to be short especially when operating under factory conditions where a long delay in bringing about gelation means the provision of storage space while gelation is taking place. The strength of the product at the point of firing is particularly important in the precision casting of intricate articles needing complicated moulds which might be damaged by rough handling. Moreover a mould of insufficient strength is liable to warp, and the avoidance of this warping is a most important problem in precision casting.

The optimum composition for the ethyl silicate seems to be about 12% by volume distilling up to 180° C. and about 48% distilling above this, under the conditions defined above, and preferably the ethyl silicate used gives results within $\pm 2\%$ of these figures. That is to say, the preferable composition is 10—14% distilling up to 180° C. and 46—50% above, or better still

11.5—12.5% distilling up to 180° C. and 47.5—48.5% above. The ethyl silicate must of course not contain such a quantity of residual hydrochloric acid remaining from its production from silicon tetrachloride as to upset this determination of its suitability. The hydrochloric acid can be removed by aeration, and the acid content should in fact preferably be less than 0.1% by weight calculated as HCl. A figure of about 0.07% is preferred.

There are various methods of obtaining an ethyl silicate of the composition needed according to the invention. One method is to react silicon tetrachloride with ethyl alcohol containing a few per cent of water under special reaction conditions which can be ascertained by a series of tests, and using for instance an adequately high temperature, an adequately short time of reaction and a sufficiency of alcohol.

An eminently suitable method of carrying out such a process is to add silicon tetrachloride and ethyl alcohol containing about 5—6% of water rapidly and simultaneously to a quantity of heated ethyl silicate of approximately the required composition serving to act as a primer for the reaction, and to supply heat to the reaction mixture. A suitable set of conditions is given in Example 1 below, and there is no difficulty in suitably adjusting the conditions once it is known that the product required is to have the characteristics defined earlier in this Specification.

Another method of obtaining the desired ethyl silicate is to take an ethyl silicate prepared from aqueous ethyl alcohol and containing an excessive quantity of the condensed silicates (as is invariably the case if special care is not taken in choosing the conditions), and adjusting the composition to that desired by adding ethyl orthosilicate which can be prepared from silicon tetrachloride and anhydrous ethyl alcohol.

The invention is illustrated by the following Examples:—

EXAMPLE 1.

An ethyl silicate of a composition within the limits defined in this Specification was prepared from ethyl alcohol and silicon tetrachloride in the manner described below.

107.6 gallons of 64 O.P. industrial methylated spirit and 71.7 gallons of silicon tetrachloride were caused to react together by adding them simultaneously and as rapidly as possible to 5 gallons of ethyl silicate having a temperature at the start of the reaction of 45° C. and employed to act as primer for the reaction. The ethyl silicate used was one having the composition indicated above as being the optimum for the purposes of the present invention, that is to say such that about 12% by volume of it

distilled up to 180° C. and about 48% above this.

Heat was supplied to the reaction vessel during the process by means of a steam jacket, though even then owing to the endothermic character of the reaction the temperature eventually dropped to a point in the neighbourhood of 10° C. When the addition of the reagents had been completed the reaction mixture was warmed to between 50 and 55° C., and the hydrochloric acid present was rapidly removed by aeration.

Aeration was continued until the content of hydrochloric acid in the mixture (calculated as HCl) was less than 0.1% by weight.

EXAMPLE 2.

A crude ethyl orthosilicate having a composition such that 65% of it by volume distilled at atmospheric pressure up to a temperature of 180° C. and 20% of it above 180° C. (under the conditions defined above) was obtained by the reaction of silicon tetrachloride with ethyl alcohol 74 O.P. and thus containing only a small amount of water.

This crude ethyl orthosilicate was used to adjust the composition of a series of samples containing an inadequate content of ethyl orthosilicate, so that the product in each instance was such that 12±2% of it distilled up to a temperature of 180° C. and 48±2% of it above 180° C.

The products were eminently suitable for use in producing refractory materials according to the invention.

EXAMPLE 3.

An ethyl silicate of a composition such that about 12% by volume distilled up to 180° C. and about 48% by volume above 180° C. using the criteria defined earlier in this Specification was employed in the production of a refractory cylinder for test purposes.

A solution was prepared by mixing together 16 cc. of 64 O.P. industrial methylated spirit and 12 cc. of an aqueous hydrochloric acid solution containing 0.6 grams of HCl per litre, and 76 cc. of the ethyl silicate were added. The mixture was shaken in a

wide-mouthed stoppered bottle until it cleared, and was then allowed to stand for an hour. A further 60 cc. of the ethyl silicate were then added.

The product was used to bind a filler of the composition

	By weight	
Fireclay	72.5%	
Charp (a calcined refractory substance consisting mainly of silica and alumina)	27.25%	60
Magnesia	.25%	

using 25 cc. of the silicate solution for each 85 grams of the filler.

In order to ascertain the gelling time, the mixture thereby obtained was poured into a cylindrical glass mould 2 inches in diameter and 1½ inches high greased with vaseline, and the time required for the mixture to set to such a degree that it did not sag under gravity when the mould was removed was determined.

A gelling time of less than 2½ hours was observed, and the cylinder when ready for firing had a satisfactory crushing strength. On firing a refractory of high quality resulted.

EXAMPLE 4.

A number of tests were made to compare the behaviour of various ethyl silicates when used as bonding agents in the production of moulds for precision casting in the manner described earlier in the Specification. In order to assess the relative merits of the different ethyl silicates, the gelling time of each of them was ascertained using the method described in Example 3, and in addition the strength of the mould prepared ready for firing was determined.

These tests were conducted on four samples as follows:—

- | | |
|--|----|
| (a) Pure ethyl orthosilicate, | 90 |
| (b) Crude ethyl orthosilicate, | |
| (c) An ethyl silicate of a composition within the limits defined according to the invention, | |
| (d) An ethyl silicate of a composition outside these limits. | 95 |

The results are given in the following table:—

Sample	Distillation Yields		Gelling Time	Mould Strength
	Up to 180° C.	Above 180° C.		
(a)	100%	Nil	300 mins.	Least
(b)	65%	25%	180 mins.	Better
(c)	9—10%	48—49%	150 mins.	Greatest
(d)	7%	68%	195 mins.	Comparable with (c)

The superiority of Sample (c) is evident from this table.

What we claim is:—

1. An ethyl silicate having a composition such that on distilling at atmospheric

pressure under the conditions hereinbefore defined 8—16% of it by volume distils up to 180° C. and 39—55% above 180° C.

2. An ethyl silicate having a composition such that on distilling at atmospheric pressure under the conditions hereinbefore defined 10—14% of it by volume distils up to 180° C. and 46—50% above 180° C. 40
- 5 3. An ethyl silicate having a composition such that on distilling at atmospheric pressure under the conditions hereinbefore defined 11.5—12.5% of it by volume distils up to 180° C. and 47.5—48.5% above 180° C. 45
- 10 4. An ethyl silicate according to Claim 1, 2 or 3, in which the acid content is less than 0.1% by weight calculated as HCl.
- 15 5. An ethyl silicate according to Claim 1, 2 or 3, in which the acid content is about 0.07% by weight calculated as HCl.
- 20 6. A process for the production of an ethyl silicate as defined in any of Claims 1 to 5, in which silicon tetrachloride is caused to react with ethyl alcohol containing a few per cent of water using an adequately high temperature and short time of reaction and a sufficiency of alcohol, the conditions being so chosen that a test shows that the required product is obtained. 50
- 25 7. A process according to Claim 6, in which silicon tetrachloride and ethyl alcohol containing about 5—6% of water are added rapidly and simultaneously to a quantity of heated ethyl silicate of approximately the required composition serving as a primer for the reaction, and heat is supplied to the reaction mixture.
- 30 8. A process according to Claim 6 or 7, in which hydrochloric acid is substantially removed from the product by aeration.
- 35 9. A process for the production of an ethyl silicate as defined in any of Claims 1 to 5, in which an ethyl silicate prepared from aqueous ethyl alcohol and containing an excessive quantity of the condensed silicates is adjusted in composition by the addition of ethyl orthosilicate. 40
10. A process for the production of an ethyl silicate substantially as described with reference to Example 1 or 2. 45
11. An ethyl silicate which has been obtained by any of the processes of Claims 6 to 10.
12. A process for the production of refractory materials, in which an ethyl silicate as defined in any of Claims 1 to 5 and 11 is used as binding agent. 50
13. A process of precision casting by the "lost wax" method, in which the refractory mould is prepared using as binding agent an ethyl silicate as defined in any of Claims 1 to 5 and 11. 55
14. A process according to Claim 12 or 13, in which hydrochloric acid is used as hydrolysing agent for the ethyl silicate. 60
15. A process according to Claim 12 or 13, in which an organic base is used as hydrolysing agent for the ethyl silicate.
16. A process for the production of refractory materials substantially as described with reference to Example 3. 65
17. Refractory materials or moulds which have been obtained by any of the processes of Claims 12 to 16. 70
18. Cast articles which have been obtained by a process of precision casting according to any of Claims 13 to 15.

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PROVISIONAL SPECIFICATION.

Improvements relating to Ethyl Silicate and to its Use in the Production of Refractory Materials.

75 We, MONSANTO CHEMICALS LIMITED, a British Company, of 8, Waterloo Place, London, S.W.1, do hereby declare the nature of this invention to be as follows:—

This invention relates to the use of ethyl silicate in the production of refractory materials, especially in precision casting, and to ethyl silicate of a special composition particularly suitable for the purpose. 95

80 Refractory materials of good quality can be obtained by mixing aqueous or more usually aqueous alcoholic ethyl silicate (to which a hydrolysing agent for the ethyl silicate has been added) with a refractory substance such as calcined fireclay to form a slurry or mix, shaping this to the desired

form, a brick or mould for instance, allowing the ethyl silicate to gel and thus harden the shaped article, and firing the product at a high temperature at which the gel is converted to silica. This appears to cement the particles of the refractory substance together to form a firm product. Attention is drawn to Specifications Nos. 575,734, 604,698, 621,737 and 639,802. 90

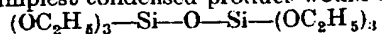
The technique is of particular value in the "lost wax" process of precision casting. 100 In this process a wax replica is made of the casting required and this is embedded in a slurry or mix of a refractory substance and the ethyl silicate, which is allowed to set round the wax by gelling of the ethyl silicate. 105

The mass is then fired to melt the wax and leave a refractory mould in which molten metal can be poured. It is not altogether necessary to use wax, and other substances, such as fusible plastics, are also suitable. An illustration of the technique is given in Specification No. 660,604, and reference is also made to Dunlop's article in the Foundry Trade Journal, 75, (1945), 107.

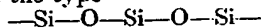
Although in this connection ethyl silicate is referred to without qualification, there are in fact a number of different chemical forms in which the ethyl silicate can be used. Ethyl silicate is normally prepared by the action of silicon tetrachloride on ethyl alcohol, and the chemical constitution of the product depends on such factors as the amount of water present when this reaction takes place. Thus if absolute alcohol is employed and the conditions are anhydrous the product will be ethyl orthosilicate of the formula



whereas if a quantity of water is present condensed products are formed, possibly owing to partial hydrolysis of the orthosilicate which may first be formed. Thus the simplest condensed product would be



and many other condensed forms containing systems of the type



are possible. If alcohol containing say 5% of water by weight is used, a mixture of ethyl silicates is formed varying from the orthosilicate to more complex condensates, each of course containing a higher proportion of silicon than the orthosilicate itself.

It has now been found that improved results are obtained in preparing the refractory materials if there is used an ethyl silicate having such a composition that on distilling at atmospheric pressure 8—16% of it by volume distills up to 180° C. and 39—55% of it above 180° C., when the distillation is continued to the point where the residue is a glue-like mass which on further heating merely breaks down to give lower boiling products. This point can readily be seen in practice by a drop in the temperature of the distilling vapours on account of these lower boiling degradation products. The fraction distilling up to 180° C. appears to be mainly ethyl orthosilicate, which boils at about 164° C., and the second fraction appears to be mainly the condensed products containing two and three silicon atoms respectively.

By using an ethyl silicate of this particular composition in the production of the refractory materials, two notable results are obtained. The gelling time of the slurry or mix containing the ethyl silicate is reasonably short, perhaps less than two and a half hours, and also a good strength is obtained

in the formed refractory material ready for firing. The precise time of gelation will of course depend on the conditions, and whether for instance the hydrolysing agent used is an acid such as hydrochloric acid (see Cogan and Setterstrom, Ind. Eng. Chem., 39, (1947), 1364) or one of the organic bases described in Specifications Nos. 575,752 and 612,622, but it is very desirable for this to be short especially when operating under factory conditions where a long delay in bringing about gelation means the provision of storage space while gelation is taking place. The strength of the product at the point of firing is particularly important in the precision casting of intricate articles needing complicated moulds which might be damaged by rough handling. Moreover a mould of insufficient strength is liable to warp, and the avoidance of this warping is a most important problem in precision casting.

The optimum composition for the ethyl silicate seems to be about 12% by volume distilling up to 180° C. and about 48% distilling above this, under the conditions defined above, and preferably the ethyl silicate used gives results within $\pm 2\%$ of these figures. That is to say, the preferable composition is 10—14% distilling up to 180° C. and 46—50% above. The ethyl silicate must of course not contain such a quantity of residual hydrochloric acid remaining from its production from silicon tetrachloride as to upset this determination of its suitability. The acid content should in fact preferably be less than 0.1% by weight calculated as HCl, say 0.07%.

There are various methods of obtaining an ethyl silicate of the composition needed according to the invention. One method is to react silicon tetrachloride with ethyl alcohol containing a few per cent of water under special reaction conditions which can be ascertained by a series of tests, and using for instance an adequately high temperature, a short time of reaction and a sufficiency of alcohol. Another method is to take an ethyl silicate prepared from aqueous ethyl alcohol and containing an excessive quantity of the condensed silicates (as is invariably the case if special care is not taken in choosing the conditions), and adjusting the composition to that desired by adding ethyl orthosilicate prepared from silicon tetrachloride and anhydrous ethyl alcohol.

The invention is illustrated by the following Examples:—

EXAMPLE 1.

An ethyl silicate of a composition within the limits defined in this Specification was prepared from ethyl alcohol and silicon tetrachloride in the manner described below.

107.6 gallons of 64 O.P. industrial methylated spirit and 71.7 gallons of silicon tetrachloride were caused to react together by adding them simultaneously and as rapidly as possible to 5 gallons of ethyl silicate having a temperature at the start of the reaction of 45° C. and employed to act as primer for the reaction. The ethyl silicate used was one having the composition indicated above as being the optimum for the purposes of the present invention, that is to say such that about 12% by volume of it distilled up to 180° C. and about 48% above this.

Heat was supplied to the reaction vessel during the process by means of a steam jacket, though even then owing to the endothermic character of the reaction the temperature eventually dropped to a point in the neighbourhood of 10° C. When the addition of the reagents had been completed the reaction mixture was warmed to between 50 and 55° C., and the hydrochloric acid present was rapidly removed by aeration.

Aeration was continued until the content of hydrochloric acid in the mixture (calculated as HCl) was less than 0.1% by weight.

EXAMPLE 2.

A crude ethyl orthosilicate having a composition such that 65% of it by volume distilled at atmospheric pressure up to a temperature of 180° C. and 20% of it above 180° C. (under the conditions defined above) was obtained by the reaction of silicon tetrachloride with ethyl alcohol 74 O.P. and thus containing only a small amount of water.

This crude ethyl orthosilicate was used to adjust the composition of a series of samples containing an inadequate content of ethyl orthosilicate, so that the product in each instance was such that 12±2% of it distilled up to a temperature of 180° C. and 48±2% of it above 180° C.

The products were eminently suitable for use in producing refractory materials according to the invention.

EXAMPLE 3.

An ethyl silicate of a composition such that about 12% by volume distilled up to 180° C. and about 48% by volume above 180° C. using the criteria defined earlier in this Specification was employed in the production of a refractory cylinder for test purposes.

A solution was prepared by mixing together 16 cc. of 64 O.P. industrial methylated spirit and 12 cc. of an aqueous hydrochloric acid solution containing 0.6 grams of HCl per litre, and 76 cc. of the ethyl silicate were added. The mixture was shaken in a wide-mouthed stoppered bottle until it cleared, and was then allowed to stand for an hour. A further 60 cc. of the ethyl silicate were then added.

The product was used to bind a filler of the composition

	By weight	
Fireclay	72.5%	70
Charp (a calcined refractory substance consisting mainly of silica and alumina)	27.25%	
Magnesia	.25%	

using 25 cc. of the silicate solution for each 85 grams of the filler.

In order to ascertain the gelling time, the mixture thereby obtained was poured into a cylindrical glass mould 2 inches in diameter and 1½ inches high greased with vaseline, and the time required for the mixture to set to such a degree that it did not sag under gravity when the mould was removed was determined.

A gelling time of less than 2½ hours was observed, and the cylinder when ready for firing had a satisfactory crushing strength. On firing a refractory of high quality resulted.

EXAMPLE 4.

A number of tests were made to compare the behaviour of various ethyl silicates when used as bonding agents in the production of moulds for precision casting in the manner described earlier in the Specification. In order to assess the relative merits of the different ethyl silicates, the gelling time of each of them was ascertained using the method described in Example 3, and in addition the strength of the mould prepared ready for firing was determined.

These tests were conducted on four 100 samples as follows:—

- Pure ethyl orthosilicate,
- Crude ethyl orthosilicate,
- An ethyl silicate of a composition within the limits defined according to the invention,
- An ethyl silicate of a composition outside these limits.

The results are given in the following table:—

Sample	Distillation Yields		Gelling Time	Mould Strength
	Up to 180° C.	Above 180° C.		
15 (a)	100%	Nil	300 mins.	Least
(b)	85%	25%	180 mins.	Better
(c)	9—10%	48—49%	150 mins.	Greatest
(d)	7%	68%	195 mins.	Comparable with (c)

The superiority of Sample (c) is evident from this table.

Dated the 16th day of September. 1949.

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